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Aluminum diffusion and reaction in thin films of perylene-3,4,9,10-tetracarboxylic dianhydride: Depth profiles and time-dependent diffusion coefficients

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Diffusion and reaction of aluminum metal species (Al) vacuum deposited on perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) thin films were investigated using angle resolved x-ray photoemission spectroscopy. The acquired data were analyzed assuming that the diffusion of Al is described by a one-dimensional diffusion equation with a time-dependent diffusion coefficient. Depth profiles and diffusion coefficients are obtained for reacted and metallic Al separately. The results show that the metallic Al diffuses rapidly during the deposition while the metal diffusion continues at a lower rate even after the deposition at room temperature. On the other hand, the reacted Al does not diffuse further into the PTCDA layers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2763980]

In organic semiconductor devices, such as electroluminescent devices, field effect transistors, and photovoltaic cells, a metal electrode is usually fabricated on an organic molecular layer by vacuum deposition. Deposited metal species are known to diffuse into the organic layer and react with the constituent organic molecules,^{1,2} which greatly affects device performances.³ Such diffusion and reaction have been examined by x-ray or ultraviolet photoemission spectroscopies for various combinations of metals and molecular organic materials.^{4,5} Since most of those experiments were made with observing spectral changes as a function of amount of deposited metal, precise values of diffusion length, or depth profile of diffused metal species are still unknown.

Although depth profiles of the metal deposited on polymer films were frequently studied,⁶ little is known on those for the metal and molecular organic layers. Previous studies include transmission electron microscopy^{3,7,8} (TEM) and sputter depth profiling.^{4,9,10} While TEM is useful to examine aggregation of metal species in an organic layer, its sensitivity is not high enough to detect metal atoms diffusing into the organic layer. The sputter depth profiling combined with various detection techniques gives a quantitative depth profile of diffused metal with high sensitivity in the range from a few tens of nanometers to a micrometer. However, the diffusion of metal species into small molecular layers is believed to occur within a few nanometers from the surface where the sputtering depth profiling does not give quantitatively reliable data.

Angle resolved x-ray photoemission spectroscopy¹¹ (ARXPS) is a technique suitable to investigate diffusion and reaction of metal species deposited on an organic layer. The probing depth analyzed by ARXPS is governed by the electron inelastic mean free path λ which is on the order of a few nanometers. The depth profiles of reacted and nonreacted metals can be separately analyzed from the chemical shifts. Unlike TEM and the sputter depth profiling, ARXPS is a nondestructive technique, and thus the time-dependent depth

profile can be obtained by repeating the measurements of the same sample specimen.

In ARXPS the signal intensity for inner shell electrons is recorded as a function of detection angle θ against the surface normal. The intensity of photoelectrons $I(p)$ can be related with the concentration of the element of interest $c(z)$ at the depth z from the surface by the Laplace transform with a parameter of $p = 1/\lambda \cos \theta$,¹² which is expressed as,

$$I(p) = A \int_0^\infty c(z) \exp(-pz) dz = \mathcal{L}[c(z); p], \quad (1)$$

where A is a constant referring to x-ray intensity, sensitivity of the detector, etc. However, due to the nature of the Laplace transform, reliable $c(z)$ cannot be derived directly from the inverse Laplace transform of the experimentally obtained $I(p)$,¹² and many algorithms for calculating $c(z)$ have been developed. In diffusion of metal into polymer layers, it is reported that a parametric model using the diffusion equation (Fick's second law) gives a good result.¹³

In this study, aluminum (Al) deposited on perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) thin films was investigated by ARXPS. By repeating the sequence of the measurements, the Al diffusion and reaction were examined as a function of time t . In the analysis of the ARXPS data, we assumed that Al diffusion is described by a one-dimensional diffusion equation. While a constant diffusion coefficient D is usually assumed in solving the diffusion equation, we instead used a time-dependent diffusion coefficient $D(t)$ that enables us to discuss time-dependent diffusion processes, e.g., metal diffusion proceeding during or after the metal deposition.

PTCDA (Tokyo Chemical Industry Co., Ltd.) was purified with three times vacuum sublimation, and thermally deposited from a resistively heated crucible at the deposition rate of 0.2–0.5 nm min⁻¹ onto a naturally oxidized silicon substrate to obtain a 25-nm-thick film. Al was deposited onto the PTCDA film at the rate of 0.1 nm min⁻¹. Three samples were prepared with different Al average thicknesses of 0.4, 1.0, and 3.9 nm; these initial thicknesses were chosen to examine the behavior of reacted, partially reacted, and mostly

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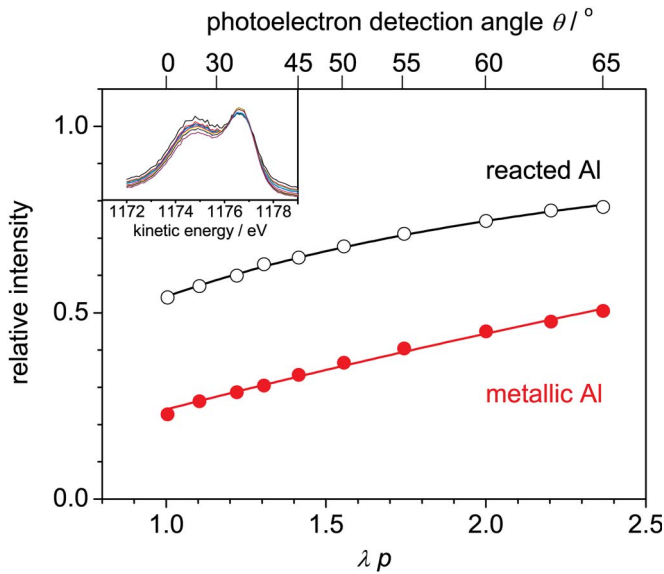


FIG. 1. (Color online) Relative intensities of reacted and metallic Al obtained from angle resolved x-ray photoemission spectroscopy (ARXPS) of the Al 2*p* core level as a function of $\lambda p = 1/\cos \theta$ with the detection angles θ . The measurements are made for the sample of the initial Al thickness of 1.0 nm about 2 h after the deposition. The lines are best fits of ARXPS intensities, assuming the Al diffusion is described by a one-dimensional diffusion equation. In the inset, the raw spectra show two peaks at low and high kinetic energies corresponding to the reacted and metallic Al, respectively.

metallic Al, respectively. The amount of the material deposited was measured with a quartz microbalance. The sample preparation and ARXPS measurements were carried out without breaking the vacuum at the pressure of 1×10^{-4} and 1×10^{-7} Pa, respectively.

ARXPS was performed on a VG Microtech ARUPS10 system equipped with a Mg *K* α x-ray source and a CLAM2 electron energy analyzer. The Al 2*p* signal was acquired at a detection angle $\theta = 5^\circ - 65^\circ$. The signal intensity was normalized to that of the C 1*s* peak from bare PTCDA at each angle θ . In the data analysis, $\lambda = 2.5$ nm is assumed for both Al and PTCDA.^{14,15} The same measurement was repeated at 2, 24, 170, 720, and 2000 h after the metal deposition. The sample was always kept at room temperature (25–30 °C) and under ultrahigh vacuum (5×10^{-8} Pa).

The spectral intensities (peak areas) of the Al 2*p* core level for the reacted and metallic Al are shown in Fig. 1 as a function of $\lambda p = 1/\cos \theta$. The data are taken at 2 h after the deposition of 1.0 nm Al. Uncertainties in the intensities were less than 3% in all the data. The raw spectra are shown in the inset of Fig. 1. Two peaks, observed at 1174.8 and 1176.6 eV in electron kinetic energy, are assigned to reacted and metallic Al, respectively.²

In order to evaluate the depth profile $c(z)$, we assume that the concentration of Al in the film depends only on the z direction (depth) and that Al diffusion is described by a one-dimensional diffusion equation,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial c}{\partial z} \right). \quad (2)$$

As diffusion coefficient D may vary during and after Al deposition, in this case, we assume that D depends only on time t . By substituting a new variable $T = Dt$, Eq. (2) can be solved under proper boundary conditions.¹⁶

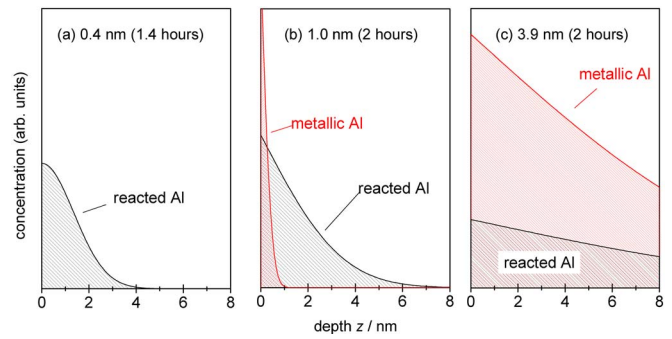


FIG. 2. (Color online) Depth profiles of reacted and metallic Al at about 2 h after the deposition. The amounts of Al initially deposited are 0.4 nm (a), 1.0 nm (b), and 3.9 nm (c) in thicknesses.

When the initial thickness of Al is small (0.4 nm), the system can be approximated as a fixed amount of diffusant α deposited on the surface to diffuse into the semi-infinite bulk. Under this boundary condition, the solution of Eq. (2) is

$$c(z) = \alpha(\pi T)^{-1/2} \exp(-z^2/4T). \quad (3)$$

On the other hand, a constant Al concentration c_0 at the surface is assumed, when the Al layer is thick enough (1.0 and 3.9 nm) and the metallic Al layer remains on the PTCDA layer. In this case, the solution is

$$c(z) = \frac{c_0}{2} \operatorname{erfc}(z/2T^{1/2}), \quad (4)$$

where erfc refers to the error function complement. In order to obtain the parameters α , c_0 , and T , the Laplace transforms of Eqs. (3) and (4) are calculated according to Eq. (1) and fitted to the experimental data using the least-squares method. Best fit lines for metallic and reacted Al are shown in Fig. 1. The obtained depth profiles of reacted and metallic Al at about 2 h after the deposition are shown in Fig. 2 for the three cases with different initial Al thicknesses.

Throughout the analyses, we assumed that the depth profiles of reacted and metallic Al are independently described by the solutions of Eq. (2). Though this is a reasonable approximation to derive the depth profiles, the diffusion coefficients for each component are mutually related through the reaction. To evaluate the diffusion coefficients $D(t)$, a diffusion equation that includes both Al diffusion and reaction must be considered. In general, such an equation will be a nonlinear differential equation and cannot be solved analytically.¹⁶ Only in a limited condition where concentration change induced by the reaction can be neglected with respect to that by the diffusion, $D(t)$ is extracted.

To evaluate $D(t)$ for the reacted Al, data from the samples of initial thickness 0.4 nm were analyzed because most of the Al is already reacted and further reaction is negligible. In the same way, the data for initial thickness of 3.9 nm were used to evaluate the diffusion of metallic Al, where most of Al remains unreacted. In these extreme cases, the diffusion constants can be obtained from the relation, $D(t) = dT/dt$.

In Fig. 3, T is plotted as a function of time t to obtain $D(t)$ from the slope of the plots dT/dt . For metallic Al, T rapidly rises at the first stage, suggesting a large diffusion coefficient during the metal deposition. As time required for one measurement of ARXPS is on the order of 1 h and longer than the time taken for Al deposition (from a few

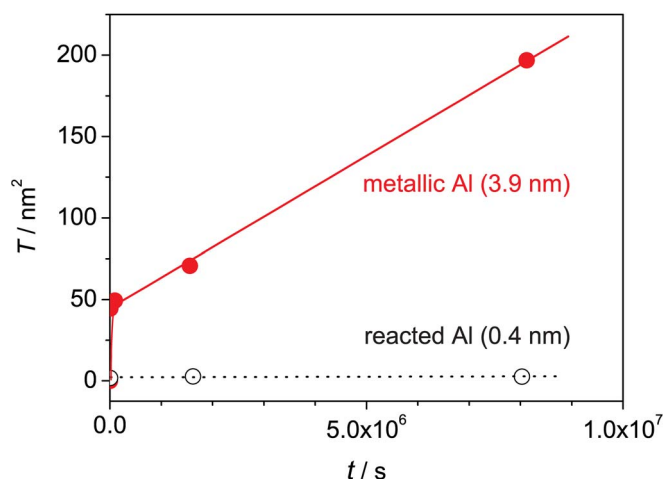


FIG. 3. (Color online) T vs t for metallic and reacted Al, for the case of initial Al thickness of 3.9 and 0.4 nm. The slope of the plot is the diffusion coefficient, $D(t)=dT/dt$.

minutes to a few tens of minutes), D cannot be determined exactly. Only the lower limit of $D > 6.2 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$ is obtained. After the deposition is completed T increases in proportional to t , which implies the diffusion of the metallic Al continues with a constant diffusion coefficient, $D = (1.5 \pm 1.0) \times 10^{-23} \text{ m}^2 \text{ s}^{-1}$.

In our experiments, we did not detect the diffusion of the reacted Al. An upper limit of the diffusion coefficient is $8 \times 10^{-26} \text{ m}^2 \text{ s}^{-1}$. This suggests that Al is immobilized due to strong chemical bond between Al and PTCDA. In this connection, an *ab initio* calculation shows that Al reacts with oxygens of carbonyl groups in naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTCDA) and forms Al_nNTCDA ($n=1-4$), where the bond energy for O–Al is 1.5–2.3 eV.¹⁷

The reaction rate for Al in PTCDA must be larger than the diffusion rate to reproduce the depth profile shown in Fig. 2(b). It seems likely that the metallic Al immediately reacts with PTCDA. This will continue until all the carbonyl oxygens form bonds with Al. Excess metallic Al further diffuses into the Al_4PTCDA layer. The diffusion and the reaction will cease only when the supply of metallic Al from the surface Al layer is extinguished.

In conclusion, diffusion and reaction of Al deposited on a PTCDA thin film were investigated using ARXPS. In the spectra, two components corresponding to metallic and reacted Al were observed. Assuming a one-dimensional diffusion equation, we obtained depth profiles of both the reacted and metallic components. Repeated ARXPS measurements after the Al deposition provided time-dependent diffusion coefficients. The results are summarized as follows:

- (1) Metallic Al diffuses into the PTCDA layer followed by reaction with PTCDA molecules.
- (2) The diffusion coefficient for metallic Al during Al deposition is larger by 10^3 than that after the Al deposition. This is consistent with a widely believed hypothesis that metal diffuses during the deposition. After the deposition, however, metallic Al continues to diffuse with constant D even at room temperature, at least during the experimental period of 3 months. The diffusion will probably continue as far as the metallic Al on the PTCDA surface remains. This behavior is important because it is closely connected with degradation at metal/organic contacts due to the metal diffusion in practical organic electronic devices.
- (3) Reacted Al does not diffuse. This reflects the strong chemical bond formation between Al and PTCDA.

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